

DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
INDIANAPOLIS

OFFICE MEMORANDUM

Date: June 10, 1997

RJH

To: C. J. Song
Modeling Section
NPDES Permitting Branch/OWM

Thru: Jan Henley, BC
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From: Syed GhiasUddin, Toxicologist
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Subject: Recalculation of Water Quality Criteria (WQC) for Iron (CAS 7439-89-6).

This correspondence replaces the Water Quality Criteria (WQC) for iron communicated to you earlier in the Inter-Office Memorandum dated October 8, 1996.

A recent literature search has shown that on iron very limited aquatic toxicity data is available. As a general rule, to calculate the WQC for iron or any other pollutant by the standard procedure toxicity data from several Genera, from at least 8 specific families from varied taxa of freshwater aquatic organisms as specified by EPA or from at least 5 specific families as specified by Indiana are required. The available aquatic toxicity data on iron do not fulfill the EPA 8 families requirements but meet the Indiana 5 families data requirements for resident species. Therefore, for calculation of aquatic WQC for iron, Indiana procedure as described in the two Indiana rules; 327 IAC 2-1-8.2 and 327 IAC 2-1-8.3 was used.

WQC for Iron:

The WQC for iron calculated using the two Indiana rules cited in the above paragraph are listed in **ATTACHMENT-I**. To calculate the WQC for iron, aquatic toxicity data was obtained from the published literature and/or from the EPA AQUIRE database. Some of these toxicity data were also used earlier by David Kallander during February 1997 to calculate the WQC for iron under the Great Lakes Initiative (GLI) guidelines adopted in January this year by Indiana (see **Page 3 for GLI WQC for iron**). Toxicity data sets from two sensitive species (*Salvelinus* or Brook trout, *Oncorhynchus* or Rainbow trout) used for criteria calculations under the GLI initiative, that are not representative of the Indiana warm waters were not included here in the WQC calculations for iron.

a. Development of an A-C Ratio for Chronic WQC: To derive a Chronic WQC, an Acute-to-Chronic Ratio (A-C Ratio) for at least one freshwater species is required by Indiana {see 327 IAC

2-1-8.3, (3) (A) (B)}. Therefore, to derive an A-C Ratio for iron, toxicity data obtained from a 21-day *Daphnia magna* chronic toxicity test conducted in Lake Superior water as the dilution water was used (see Biesinger, K.E. and Christensen, J. M., Fish. Res. Board, Canada, 29 (12), 1691-1700, 1972). Historically, for WQ criteria development Reconstituted/Synthetic Laboratory water is used as the dilution water. However, using an acceptable Surface water (from pristine Lakes, Streams and Rivers, Ground water or even tap water) as the dilution water in aquatic toxicity tests is recommended by EPA and is not unusual to use even in toxicity tests for the WQC development. Instances of such occurrence and use of acceptable surface water in WQ criteria development can be found in the EPA criteria documents.

The following are the acute and chronic toxicity test results on iron obtained from the scientific paper by Biesinger and Christensen, 1972 that were used to develop an A-C Ratio for iron:

Acute and Chronic Toxicity Test Results of Iron in Lake Superior Water

| Species | LC ₅₀ | IC ₁₆ | A-C Ratio (LC ₅₀ /IC _p) |
|----------------------|-----------------------------|------------------|---|
| <i>Daphnia magna</i> | 9600 (48-hr) (With Food) | 4380 | 2.2 |
| | 5900 (21-day) | 4380 | 1.35 = 2.00 |

For the calculation of WQC from toxicity test with Daphnids, a 48-hr LC₅₀ is recommended. However, according to EPA (see 1985 National Guidance on criteria development) under certain circumstances and acceptable control animals a LC₅₀ from a longer test duration could be used to derive a WQ criterion.

i. **Discussion of *Daphnia magna* Life-Cycle Toxicity Test Results:** To develop an A-C Ratio, an acute sensitive endpoint (LC₅₀) is recommended. Among the two LC₅₀ values for *Daphnia magna* reported by Biesinger and Christensen (1972), 21-day LC₅₀ (5900 ug/L) is the lowest and the most sensitive acute endpoint which gives an A-C Ratio of 1.35. This A-C Ratio is lower than the A-C Ratio of 2.2 which was derived from a 48-hr LC₅₀ wherein the organisms were fed during the test period. But test results from such acute toxicity tests wherein organisms are fed are not generally recommended by EPA to be used in calculations of WQ criteria. As a result the other A-C Ratio (1.35) appears good and acceptable, but even this A-C Ratio can not be used because it is lower than the minimum A-C Ratio of 2 required by EPA. In such circumstances EPA recommends to raise the A-C Ratio to 2 (see 1988 EPA 1988 Aluminum Criteria Document and 1985 National Guidance on WQC development).

Based on the comparison of two LC₅₀ values listed above for *Daphnia* and the options available, it was assumed that feeding of Daphnids during the test did not effect the acute toxicity of iron. The 48-hr LC₅₀ (9600 mg/L) for *Daphnia* as expected was higher than the 21-day LC₅₀ (5900 mg/L), and the A-C Ratio (2.2) derived from the 48-hr acute value (LC₅₀ 9600 ug/L) could be used in

criteria development for iron.

One other thing, in the above toxicity data **ICp (Percent Inhibitory Concentration)** instead of the usual **NOEC (No Observed Effect Concentration)** and **LOEC (Low Observed Effect Concentration)** was used to derive the chronic value for development of A-C Ratio. ICp for low level or sub-chronic effects for up to 25% is now being recommended as the chronic endpoint over the NOEC and LOEC for development of chronic value and the A-C Ratio. The reason, the ICp is based on statistical method around which confidence limits could be derived versus the NOEC or LOEC values which could not be any true hard numbers with no confidence limits. This new approach of using ICp as the chronic endpoint has been recommended in several EPA documents for whole effluent toxicity tests and more recently in the EPA Site-specific WQC development document (see "**Interim Guidance on Determination and Use of Water-Effect Ratios for Metals**", EPA-823-B-94-001, February 1994).

b. WQC For Iron Calculated for the Protection of Aquatic Life: For comparison, the WQC for iron calculated using the existing Indiana rules and the GLI guidance are listed below.

WQC For Iron For the Protection of Aquatic Life

| | Using Indiana Existing Rules | Using GLI Guidance (2/97) |
|-------------------------|---------------------------------|---------------------------------|
| Chronic (CAC) | = 2495 ug/L (2.5 mg/L) | 16 ug/L (0.016 mg/L) |
| Acute (AAC) | = 2744 ug/L (2.7 mg/L) | 143 ug/L (0.143 mg/L) |
| Final Acute Value (FAV) | = 5488 ug/L (5.5 mg/L) | 286 ug/L (0.286 mg/L) |

From comparison of the two sets of WQC for iron, it appears that WQC for iron calculated under the existing Indiana rules are relatively less stringent as compared to the ones derived under the GLI guidance. One reason, for Indiana warm waters, unlike in calculation of WQC for iron under the GLI guidance for the Great Lake basin (Tier-2), the lowest SMAV for the cold water species (Brook trout, Genus *Salvelinus*) was not used (see ATTACHMENT-1).

The WQC for iron calculated using the two existing Indiana rules could be used across Indiana other than the Great Lake basin where the WQC derived from GLI guidance would be more appropriate and applicable.

cc: Steve Roush
Dennis Clark
David Kallander

PS: This memorandum confirms to E-mail correspondence on WQC for iron forwarded to Steve Roush in the Industrial NPDES Permits Section on March 19 and 20, 1997.

ATTACHMENT-1

Recalculation of WQC for Iron (CAS # 7439 - 89 - 6)

| Genus | GMAV (LC ₅₀ /EC ₅₀ : ug/L) | Rank | Cum. Prob. P (Rank/n+1) | Sq.Rt. (P) | ln (GMAV) | ln (GMAV) ² |
|-------------------|---|------|----------------------------|------------|-----------|------------------------|
| <i>Ictalurus</i> | > 500,000 | 10 | | | | |
| <i>Asellus</i> | 124,000 | 9 | | | | |
| <i>Crangonyx</i> | 120,000 | 8 | | | | |
| <i>Poecilia</i> | 117,000 | 7 | | | | |
| <i>Tubifex</i> | 101,000 | 6 | | | | |
| <i>Carassius</i> | > 40,000 | 5 | | | | |
| <i>Orconectus</i> | 32,000 | 4 | 0.3636 | 0.6030 | 10.3735 | 107.6095 |
| <i>Gambusia</i> | 26,000 | 3 | 0.2727 | 0.5222 | 10.1659 | 103.3455 |
| <i>Pimephales</i> | 18,670 | 2 | 0.1818 | 0.4264 | 9.8347 | 96.7213 |
| <i>Daphnia</i> | 7,300 | 1 | 0.0909 | 0.3015 | 8.8956 | 79.1317 |
| Summation (E) | | | 0.9090 | 1.8531 | 39.2697 | 386.8080 |

| | | | | | | |
|--------------------------|---|-----------|---|---|--------|--|
| T | = | 4 | | | | |
| E ln (GMAV) | = | 39.2697; | S | = | 5.0359 | |
| E ln (GMAV) ² | = | 386.8080; | L | = | 7.4844 | |
| E P | = | 0.9090; | A | = | 8.6104 | |
| E Sq. Rt. (P) | = | 1.8531; | | | | |

A-C Ratio = 2.2 (see Biesinger and Christensen 1972).

Recalculated WQC For Iron: (See Next Page for Details)

| | | |
|---------------------------------|---------------------------|-------------|
| Final Acute Value (FAV) | = e ^A (8.6104) | = 5488 ug/L |
| Acute Aquatic Criterion (AAC) | = FAV/2 | = 2744 ug/L |
| Chronic Aquatic Criterion (CAC) | = FAV / 2.2 (A-C Ratio) | = 2495 ug/L |

The following genera were omitted from the available Aquatic toxicity database to Recalculate the WQC for Iron:

| | GMAV | Sensitivity Rank |
|-----------------------|--------|------------------|
| o <i>Salvelinus</i> | 1,750 | 1 |
| o <i>Oncorhynchus</i> | 18,300 | 2 |

WQC Calculations Details:

$$S^2 = \frac{E \{ (\ln \text{GMAV})^2 \} - E \{ (\ln \text{GMAV}) \}^2 / T}{E(P) - E \{ (\sqrt{P}) \}^2 / T}$$

$$S^2 = \frac{E \{ (\ln 386.8080)^2 \} - E \{ (\ln 39.2697) \}^2 / 4}{E(0.9090) - E \{ (\sqrt{1.8531}) \}^2 / 4}$$

$$= \frac{386.8080 - 385.5273}{0.9090 - 0.8585}$$

$$= \frac{1.2807}{0.0505} = \sqrt{25.3604}; \quad S = 5.0359$$

$$L = \{ E(\ln \text{GMAV}) - S(E(\sqrt{P})) \} / T$$

$$\begin{aligned} L &= \{ (39.2697) - 5.0359 \times 1.8531 \} / 4 \\ &= \{ 39.2697 - 9.3320 \} / 4 \\ &= 29.9377 / 4 \\ &= \mathbf{7.4844} \end{aligned}$$

$$A = S\sqrt{(0.05)} + L$$

$$\begin{aligned} A &= 5.0359 \times 0.2236 + 7.4844 \\ &= 1.1260 + 7.4844 \\ &= \mathbf{8.6104} \end{aligned}$$

$$\begin{aligned} \text{FAV} &= e^A \\ &= e(8.6104) = \mathbf{5488 \text{ ug/L}} \end{aligned}$$

From: SYED GHIAUDDIN
To: BRUNO PIGOTT; GERNAND, MATT; HESS, CATHERINE; STEVE ROUSH
Date: 3/24/05 10:21AM
Subject: Site-Specific WQC for Aluminum

Matt Gernand

Attached, please find an **Update** on **Site-Specific WQC for Aluminum** recalculated by IDEM in 2005 for Indiana warm waters outside the Great Lakes Basin. This should also serve as a response and comments to ALCOA's submittal on this topic from Lafayette and Warrick, Indiana, in a meeting at IDEM on November 3, 2004 followed by hard copies of the same to IDEM on November 5, 2004.

The new set of Aluminum WQC recalculated in 2005 will replace the Site-Specific WQC for Aluminum that were recalculated by IDEM in 2002. As a result of this recalculation, the new WQC for Aluminum have become more conservative as compared to the earlier ones. (FAV = 1974, AAC = 987 and CAC = 174 ug/L versus FAV = 1986, AAC = 993 and CAC = 174 ug/L derived in 2002). This new set of WQC are based on toxicity data from **12 Genera, 13 species** instead of toxicity data from **11 Genera, 12 species** used by IDEM earlier; See **WQC Summary Table 2, Discussion/Conclusions** and **Table 3** of the attached document for criteria calculations details and explanations.

The WQC for Aluminum recalculated by ALCOA (FAV = 2107.52, AAC = 1053.57 and CAC = 439.86 ug/L) derived from toxicity data obtained from **13 Genera, 14 species** are not acceptable. The various reasons and explanations for not approving the WQC for Aluminum calculated by ALCOA are discussed and listed on pages 3 and 4 of the attached document.

Please contact Dennis Clark and/or me at 317/308-3180, if you have any questions.

Thank You/Ghias

CC: DENNIS CLARK; GARCEAU, ART; GARY PAVICH; JOHN ELLIOTT; LEE BRIDGES;
STAN RIGNEY; STENNER, BILL

SITE-SPECIFIC WATER QUALITY CRITERIA (WQC) FOR ALUMINUM: 2005-An UPDATE

National Water Quality Criteria (WQC)

WQC for Aluminum (Al): The so called original State or National acute and chronic WQC for Aluminum (Al) are based on acute toxicity data from **14 Genera or Genus Mean Acute Values (GMAVs)** from **15 species of aquatic organisms** and a default Acute-to-Chronic (A-C) Ratio of 2. The U.S. EPA calculated **Final Acute Value (FAV)**, **Acute Aquatic Criterion (AAC)**, and **Chronic Aquatic Criterion (CAC)** were as follows:

FAV = 1,496 ug/L, (> 1,986 ug/L FAV calculated by IDEM in 2002)

AAC = 748 ug/L, (> 993 ug/L AAC calculated by IDEM in 2002)

CAC = 87 ug/L, (Lowered to by U.S. EPA from calculated chronic criterion of 748 ug/L).

Since the U.S. EPA Chronic WQC (CAC) calculated from FAV and the A-C Ratio of 2 (FAV = 1,496 ug/L/2), was similar to acute criterion and relatively high (748 ug/L) as compared to the Aluminum concentrations which produced toxic or biological effects in Striped bass (*Morone saxatilis*) and Brook trout (*Salvelinus fontinalis*), the calculated chronic criterion value was lowered to 87 ug/L by U.S.EPA to protect the two species (see 1988 EPA Aluminum Criteria Document).

pH Effect and Aluminum Toxicity: The WQC for Aluminum were calculated by U.S. EPA from toxicological data obtained at a pH that ranged between 6.5 and 9.0. Toxicity of Aluminum is speculated to be related to pH and most of this information comes from toxicity studies in Rainbow trout (Salmonid, a Cold-water fish) wherein toxicity of Aluminum increased as the pH of the dilution water increased from 6.8 to 8.99 (7.00 to 9.00). However, in some studies with Rainbow trout and Fathead minnow (FHM) an opposite relationship (Aluminum more toxic at lower pH) was found by several investigators. Furthermore, no definitive data are available concerning the effect of pH on toxicity of Aluminum to invertebrates to validate or repudiate one or the other pH effect on Aluminum toxicity.

Site-Specific WQC Calculated by IDEM in 2002

Realizing that National chronic aquatic criterion (CAC) for Aluminum (87 ug/L) is very restrictive and not applicable to Indiana warm waters, in 2002 Indiana utilizing the provisions in the Indiana Rule 327 IAC 2-1-8.2, had recalculated site-specific WQC for Aluminum. At this time the site-specific acute and chronic WQC for Aluminum were calculated by IDEM using the GMAVs from **11 Genera from 12 species** after eliminating toxicity data for 3 Salmonids species (*Oncorhynchus*, *Salmo* and *Salvelinus*, see Table 1, Rows 1 through 3) that were not resident or occur at the site in Indiana warm waters, and using a **default A-C Ratio of 2** same as used by the U.S. EPA. As a result of this modification and criteria calculations, the new data set had resulted in a site-specific FAV of 1986 ug/L, an acute criterion of 993 ug/L (FAV/2) and a chronic

criterion of 993 ug/L (FAV/Default A-C Ratio of 2) for Aluminum, see WQC Summary Table 2, Rows 1 and 2 for EPA and IDEM calculated Aluminum criteria.

As we know chronic criterion has to be lower than the acute criterion. Since both recalculated acute and chronic criteria came out as equal numbers (993 ug/L) just as the 748 ug/L for acute and chronic criteria calculated by U.S. EPA, the calculated chronic criterion of 993 ug/L was lowered to at best 174 ug/L (to protect surrogates of Stripped bass-*Morone chrysops* and Largemouth bass- *Micropterus species* etc.), just as the U.S. EPA had lowered the calculated chronic criterion of 787 ug/L to 87 ug/L to protect Brook trout (*Salvelinus fontinalis*) and Stripped bass (*Morone saxatilis*).

It must be mentioned, the U.S. EPA had used the toxicity data for Stripped bass and Brook trout from a 7- day test at pH 6.5 - 6.6, but Indiana used toxicity data for Stripped bass and Largemouth bass from pH of 7.2 - 7.8 which was within the pH range of ambient waters. All of this data and much more listed in Table 6 of the 1988 Aluminum Criterion Document are summarized in this document as a footnote to WQC Summary Table 2. Additionally, it must be mentioned, at a pH of 7.2 - 7.8 in a 7-day test, Largemouth bass had an EC₅₀ of 170 ug/L, at a pH of 7.4 in a 7-day test Goldfish and Narrow-mouthed Toad had an EC₅₀ of 150 and 50 ug/L, respectively. Indiana also knows that surrogates of Stripped bass- White bass (*Morone Chrysops*), Largemouth bass (*Micropterus Sp.*) etc., are also present in warm waters of Indiana/Midwest and beyond and these need to be protected. Based on this Indiana felt comfortable with the Site-specific WQC for Aluminum (Al) derived in 2002 from 11 Genera from 12 species, FAV= 1986, acute criterion = 993 ug/L and chronic criterion = 174 ug/L (Lowered from calculated chronic criterion of 993 ug/L) that would be protective of aquatic life in warm waters.

TABLE 1
Aquatic Organism Deleted or Added for Site-Specific WQC Calculations

Aquatic Organisms not Representative of Indiana Warm Waters Eliminated (-) or Aquatic Organism Expected to be Present Added (+) to the National Database for Calculation of Site-Specific WQC for Aluminum.

| Species | Common Name | SMAV | GMAV | Sensitivity Rank |
|--|----------------|----------|----------|------------------|
| 1. <i>Oncorhynchus tshawytscha</i> (-) | Chinook salmon | > 40,000 | > 40,000 | 10 |
| 2. <i>Salmo gairdneri</i> (-) | Rainbow trout | 10,390 | 10,390 | |
| 3. <i>Salvelinus fontinalis</i> (-) | Brook trout | 3,600 | 3,600 | 2 |
| 1. <i>Crangonyx pseudogracilis</i> (+) | Amphipod | 9,190 | 9,190 | 2 |

SMAV = Species Mean Acute Value; GMAV = Genus Mean Acute Value

Site-Specific WQC Calculated by ALCOA in 2004

Recently (in 2004), ALCOA from Lafayette and Warrick, Indiana, had recalculated the Site-Specific WQC for Aluminum using the same 11 Genera from 12 species as IDEM did in 2002 and also after making correction to the acute toxicity data from *Dugesia* species (>16,600 instead of >23,000 in the original EPA Criteria Document). But these recalculations had resulted in relatively lower criteria values than the ones calculated by IDEM in 2002. The Aluminum criteria derived by ALCOA using the above described approaches were as follows:

FAV = 1,882.4 ug/L, (< 1,986 ug/L FAV calculated by IDEM in 2002)
AAC = 991.2 ug/L, (< 993 ug/L AAC calculated by IDEM in 2002)
CAC = -

FAV = 1,978.6 ug/L, (< 1,986 ug/L FAV calculated by IDEM in 2002)
AAC = 989.3 ug/L, (< 993 ug/L AAC calculated by IDEM in 2002)
CAC = -

see WQC Summary Table 2, Rows 7 and 8.

Realizing the Aluminum criteria values were not sufficient and helpful to ALCOA, ALCOA took additional steps to research the literature on Aluminum and gathered additional toxicity data on Aluminum after the WQC for Aluminum were developed in 1985 and published in 1988 by U.S. EPA. From this endeavor, ALCOA had added toxicity data from two more species (*Crangonyx pseudocialis* and *Tubifex tubifex*) from Martin and Holdich 1986 and Khangarot and 1991 publications), modified the existing toxicity for *Daphnia magna* by adding new acute toxicity data by Khangarot and Ray 1989 and corrected the acute toxicity data for *Dugesia tigrina* as before.

Furthermore, for calculation of chronic criterion for Aluminum, in one set of calculations ALCOA used a default A-C Ratio of 2 same as used by EPA and IDEM, and in another set instead of an A-C Ratio of 10.64 for Fathead minnow (FHM) from the Aluminum Criteria Document, a Geometric mean A-C Ratio of 4.79 derived from Survival and Growth endpoints from a 28-day FHM chronic toxicity test obtained from an Unpublished Report by Kimball (Year - ?) was used. Additionally, ALCOA for some unexplained reasons did not use the A-C Ratio of 51.47 from *Daphnia magna* reported in the 1988 Aluminum Criteria document.

The Aluminum criteria derived by ALCOA using toxicity data from 13 Genera from 14 species and the approaches described above were:

FAV = 2,107.52 ug/L, (> 1,986 ug/L FAV calculated by IDEM in 2002)
AAC = 1,053.76 ug/L, (> 993 ug/L AAC calculated by IDEM in 2002)
CAC = 1,053.76 ug/L, (> 993 ug/L CAC calculated by IDEM using 2 as the A-C Ratio)
CAC = 439.86 ug/L, (> 174 ug/L CAC, Lowered to by IDEM in 2002).

see WQC Summary Table 2, Rows 9 and 10.

While IDEM aggress with ALCOA to add *Crangonox* data and correct the acute toxicity data for the *Dugesia Sp.* to the database, but the Site-Specific criteria for Aluminum calculated by ALCOA are unacceptable for the following reasons and the same reasons are also in concurrence to the recent discussion with the U.S. EPA:

- i. Toxicity data for *Daphnia magna* and *Tubifex tubifex* are unacceptable because the Aluminum salt used for testing contained ammonia and data from such studies should not be used in criteria calculations.
- ii. As per discussions with U.S. EPA, in the *Daphnia magna* test by Khangarot and Ray (1989), the DO of the well water used was 49.3% some of the time and it might have been even lower sometimes during the test.
- iii. A Geometric mean Acute-Chronic (A-C) Ratio of 4.79 as suggested by ALCOA derived from FHM 28-day chronic toxicity test obtained from Survival and Growth endpoints is unacceptable. An A-C Ratio of 10.64 obtained from the FHM Growth sensitive endpoint in the same test as reported by EPA is the correct one (see Unpublished Report by Kimball).
- iv. ALCOA had used the A-C Ratio obtained from just the FHM species and did not use the A-C Ratio of 51.47 for *Daphnia magna* for some unexplained reasons. A critical review of the Un-published Kimball's Manuscript has shown that the test results from a 28-day life cycle chronic toxicity test are acceptable and the A-C Ratio of 51.47 for *Daphnia* derived for the Reproduction sensitive endpoint is valid to both EPA and IDEM.

As per EPA's General Guidance for criteria development, A-C Ratios for a number of species that are within a factor of 10, should be combined and a geometric mean of all the A-C Ratios should be calculated. The 4.79 A-C Ratio for FHM calculated by ALCOA differ by a factor of >10 from the acceptable A-C Ratio of 51.47 for *Daphnia magna*, and so this could not be combined with the 51.47 A-C Ratio for *D. magna* or used in criteria calculations. Moreover, an acceptable A-C Ratio must come from a sensitive species such as *Ceriodaphnia Sp.*, (Sensitivity Rank 1) and not from FHM that has a Sensitivity Rank of 7 (see Table 3 for Species Sensitivities). Since the 4.79 A-C Ratio recalculated by ALCOA comes from a single relatively insensitive species (FHM), therefore this could not be readily used in criteria calculations.

Besides, instead of using a default A-C Ratio of 2, both U.S. EPA and IDEM could have used either or combined A-C Ratios of 10.64 and 51.47 from FHM and *D. magna*, but this was not done so. If either of the above A-C Ratios for FHM and/or *D. magna* were used by IDEM for chronic criteria calculations, individually or as Geometric mean A-C Ratio of 23.4, using the FAV value (1986 ug/L) calculated by IDEM in 2002 this would have resulted in Aluminum chronic criterion of 187 ug/L (1986/10.64), 39 ug/L (1986/51.47) or 85 ug/L (1986/23.4), respectively. On the same token, using the FAV value (1496 ug/L) developed by U.S. EPA, the respective Aluminum chronic criterion values would have been 141 ug/L (1489/10.64), 29 ug/L (1496/51.47) or 64 ug/L (1496/23.4), respectively.

- v. Last but not the least, irrespective of how the Aluminum chronic criterion is derived, the recalculated chronic criterion for Aluminum, 1053.76 ug/L or the 439.86 ug/L (439.98 ug/L) derived by using a default A-C Ratio of 2 or an unacceptable A-C Ratio of 4.79, the calculated chronic criterion for Aluminum was not lowered by ALCOA to 174 ug/L. From IDEM's perspective for protection of aquatic life, chronic criterion for Aluminum has to be lowered to at least 174 ug/L to protect surrogates of Stripped bass (*Morone chrysops*), Largemouth bass (*Micropterus Sp.*) and Goldfish (*Carrassius Sp.*) etc., that are present in warm waters in Indiana/Midwest and beyond.

Site-Specific WQC Calculated by IDEM in 2005

Based on the above analysis and after having discussions this year with the U.S. EPA staff in Region 5, in Chicago, IL, Duluth, MN., and from EPA Headquarters in Washington, regarding various issues with Aluminum criteria, especially about the A-C Ratios and which new acute toxicity data for Aluminum are acceptable for criteria calculations, IDEM had lowered the *Dugesia Sp.*, acute numbers from >23,000 to >16,600 ug/L and added toxicity data for one more species (*Crangonyx Sp.*, Acute value 9,190 ug/L) to the Site-Specific toxicity database and once again recalculated the Site-Specific WQC for Aluminum. This recalculation using toxicity data from 12 Genera from 13 species has resulted in WQC for Aluminum as follows:

FAV = 1,974 ug/L, (> 1,986 ug/L FAV calculated by IDEM in 2002)

AAC = 987 ug/L, (> 993 ug/L AAC calculated by IDEM in 2002)

CAC = 174 ug/L, (Lowered to by IDEM from calculated chronic criterion of 987 ug/L).

see WQC Summary Table 2, Row 5 and Table 3 for criteria calculation details.

A complete list of Salmonids and *Crangonyx* (with the respective SMAV, GMAV and the Species Sensitivity Rank) that were eliminated or added to the toxicity database for recalculation of WQC for Aluminum by IDEM in 2005 are listed in Table 1.

Discussion:

As can be seen from criteria calculations for Aluminum, in either attempt back in 2002 or now in 2005, the IDEM's recalculated Site-Specific WQC for Aluminum are above the WQC developed by EPA. This is true for FAV (1986 ug/L or 1974 versus 1496 ug/L by EPA), acute criterion (993 ug/L or 987 ug/L versus 748 ug/L by EPA) and especially, the chronic criterion (174 ug/L) which is at least twice the 87 ug/L chronic criterion proposed by U.S. EPA in the 1988 Aluminum Criteria Document.

In Indiana warm waters many species of Isopods from Genus *Asellus* are present. According to Indiana Rule 327 IAC 2-1-8.2 (2)(B), "If data are not available for resident species, data from non-resident species may be substituted and will be assumed to be representative of resident species". On this basis and to protect other species of *Asellus*, besides the *Crangonyx* species 96-hr acute toxicity data (9,190 ug/L), if IDEM was also to include in criteria calculations the available acute toxicity data (72-Hr. LC₅₀ 4,370 ug/L) for a non-resident species- *Asellus aquaticus*, from the same publication by Martin and Holdich 1986, the Aluminum criteria as compared to the ones calculated in 2005 or in 2002 would have been more restrictive (FAV = 1743 ug/L, AAC = 872 ug/L, CAC = 174 ug/L (Lowered to from calculated 872 ug/L)), see WQC Summary Table 2, Row 6.

According to the Recalculation Procedure and General Guidance on criteria development, if the SMAV for a commercially or recreationally important species is lower than the calculated FAV, then that SMAV should be used as the Final Acute Value (FAV).

Illustration of such criteria calculations using SMAV from a 7-day test for Largemouth bass (EC₅₀, 170 ug/L), Goldfish (EC₅₀, 150 ug/L) and Narrow-Mouthed toad (EC₅₀, 50 ug/L) is shown in WQC Summary Table 2, Row 4. On the same token, instead of using a default A-C Ratio of 2, if the Geometric mean A-C Ratio of 23.4 derived from *Daphnia* and FHM were used, the chronic criterion for Aluminum would have been even more restrictive (84.87 ug/L), see WQC Summary Table 2, Row 3. It is well known that criteria for Aluminum are problematic and if EPA and IDEM had followed either of these approaches, the criteria for Aluminum would have become more stringent.

Conclusions:

1. In 2005, IDEM has recalculated a new set of Site-Specific WQC for Aluminum for Indiana warm waters by deleting the cold water species that are not representative of warm waters and also by adding new toxicity data for *Crangonyx Sp.*, besides correcting the acute toxicity data numbers for *Dugesia Sp.* These new criteria for Aluminum take into account the acceptable toxicity data currently available for Aluminum and are based on toxicity data from 12 Genera from 13 species instead of toxicity data from 11 Genera from 12 species used in criteria calculations by IDEM in 2002. Therefore, the newly derived Site-Specific WQC for Aluminum derived by IDEM in 2005 will replace the old set of Site-Specific WQC for Aluminum calculated by IDEM back in 2002. The Site-Specific WQC for Aluminum developed by IDEM in 2002 and 2005 are listed below.

Year and Site-Specific WQC Calculated by IDEM for Aluminum (ug/L)

| Year | Final Acute Value (FAV) | Acute Criterion (AAC) | Chronic Criterion (CAC) | A-R Ratio |
|----------|----------------------------|--------------------------|----------------------------|--------------|
| 2002 | 1,986 | 993 | 993 (174.00) | 2 (1) |
| 2005 (✓) | 1,974 (✓) | 987 (✓) | 987 (174.00)* (✓) | 2 (1) |

/* Chronic Criterion (CAC): 174.00 ug/L, see Table 3 and text for details.

2. The U.S. EPA is aware of the various issues related to the Aluminum WQC and is considering holding a consortium of Aluminum Stakeholders to fix the Aluminum criteria issues, but until then the Site-specific WQC for Aluminum calculated by IDEM in 2005 would be applicable for most if not all warm waters in Indiana outside the Great Lakes Basin.

End

March 24, 2005

WQC SUMMARY TABLE 2

Water Quality Criteria (WQC) for Aluminum (Al)

The following is a review of the Regular and Site-Specific WQC (ug/L) for Aluminum calculated by U.S. EPA, IDEM and ALCOA:

| Organization | Genera Used (No.) | FAV (FAV/2) | AAC (FAV/A/C Ratio) | CAC | A/C Ratio |
|------------------------------------|----------------------|------------------------|------------------------|-------------------------|--------------------|
| U.S. EPA/Regular | 14 | 1496 (pH 6.5 – 9.0) | 748 | 748 (87.00) | 2 (1) (Default) |
| IDEM/Site-Sp. | 11 (2002) | 1986 | 993 | 993 (174.00) | 2 (1) (Default) |
| IDEM/Site-Sp. | 11 | 1986 | 993 | < 84.87 (87 or 174) | 23.4/@ |
| IDEM/Site-Sp. | 11 | 170/150 → | 85/75 | 85/75 (50) | 2 (1) |
| IDEM/Site-Sp. (✓) | 12 (2005) | 1974 (✓) | 987 (✓) | 987 (174.00) (✓) | 2 (1) (Default) |
| IDEM/Site-Sp. | 13 | 1743 | 872 | 872 (174.00) | 2 (1) |
| IDEM/Site-Sp. (Recal. By Alcoa) | 11 | 1982.4 | 991.2 | - | - |
| IDEM/Site-Sp. (Recal. By Alcoa) | 11 | 1978.6 | 989.3 | - | - |
| ALCOA/Site-Sp. (Proposed) | 13 | 2107.52 | 1053.76 | 1053.76 | 2 (1) (Default) |
| ALCOA/Site-Sp. (Proposed) | 13 | 2107.52 | 1053.76 | 439.86 (439.98) | 4.79/* |

/@ A/C Ratio (23.4) = Geometric mean of 51.47 and 10.64 for *Daphnia* and FHM versus 0.9958 (1) for *Ceriodaphnia dubia*

/* A/C Ratio (4.79) = Geometric mean of 6.034 + 3.804 for FHM for Growth & Survival (Kimball ?). Each A/C Ratio was derived by ALCOA from an **Unpublished Report by Kimball (LC50/MATC for FHM; 35000/5800 and 35000/9200)**, that was not used by U.S. EPA in the 1988 Aluminum Criteria Document.

| 1. Striped bass/ <i>Morone</i> Sp. data: (see 1988 EPA Aluminum Criteria Document) (160-Days/7 Days Duration) | pH | Effect | Conc. ug/L |
|--|------------|------------------------------|------------------|
| | 6.5 | 0% dead | 87.2 |
| | 6.5 | 58% dead | 174.4 |
| | 7.2 (IDEM) | 2% dead | 174.4 (IDEM) |
| | 7.2 | 100% dead | 348.8 |
| 2. Largemouth bass/ <i>Micropterus</i> Sp. | 7.2-7.8 | 50% dead (EC ₅₀) | 170.0 (D/8 Days) |
| 3. Goldfish/ <i>Carrassius</i> Sp. | 7.4 | 50% dead (EC ₅₀) | 150.0 (D/7 Days) |
| 4. Narrow-mouthed toad/ <i>Gastrophryne</i> | 7.4 | 50% dead (EC ₅₀) | 50.0 (D/7 Days) |

Note:

1. According to EPA, Freshwater FAV for Aluminum was calculated at a pH between 6.5 and 9.0. EPA lowered the calculated chronic criterion -CAC ((748 ug/L) to 87 ug/L Al that had 0% effect at pH 6.5 to protect Brook trout and Striped bass. In Brook trout 88 ug/L Al had 4% reduction in the weight in a 60-day test.

2. IDEM did not use the Striped bass data at pH 6.5 and 6.6 as indicated in the ALCOA data sheet report. IDEM lowered the calculated CAC (993 ug/L) to 174 ug/L AI that had 2% effect at pH 7.2 to protect White bass (*Morone chrysops*), Largemouth bass and Smallmouth bass etc., as surrogates of Striped bass that occur widely distributed in Indiana/Midwest and beyond.
3. According to the EPA's 1994 Recalculation Procedure for Site-specific water quality criteria (WQC), "if the variety of aquatic invertebrates, amphibians and fishes, is so limited that species in fewer than eight families occur at the site, the general Recalculation Procedure is not applicable and the following version of the Recalculation Procedure must be used:
 - i. Data must be available for at least one species in each of the families that occur at the site.
 - ii. The lowest Species Mean Acute Value that is available for a species that occurs at the site must be used as the FAV.
 - iii. The site-specific CMC and CCC must be calculated as described below in part 2 of Step E, ---- " (from eight family data).

The statement in item #ii above is similar to in the EPA's General Guidance on WQC development. It states that if the SMAV of a commercially or recreationally important species is lower than the calculated Final Acute Value (FAV), then that SMAV should be used as the Final Acute Value instead of the calculated FAV.

4. Alternatively, as per the EPA's 1994 Recalculation Procedure Guidance on water quality criteria (WQC), "The calculated FAV, CMC, and / or CCC must be lowered, if necessary, to (1) protect an aquatic plant, invertebrate, amphibian, or fish species that is a critical species at the site ----".

TABLE 3
Recalculation of Site-Specific WQC for Aluminum (Al), 2005

| Genus | GMAV (ug/L) | Rank | Cum. Prob. P = (Rank/n+1) | Sq.Rt. (P) | ln (GMAV) | ln (GMAV) ² |
|---------------------|----------------|------|------------------------------|------------|-----------|------------------------|
| <i>Tanytarsus</i> | >79,000 | 12 | | | | |
| <i>Lepomis</i> | >50,000 | 11 | | | | |
| <i>Perca</i> | >49,000 | 10 | | | | |
| <i>Ictalurus</i> | >47,000 | 9 | | | | |
| <i>Daphnia</i> | 38,200 | 8 | | | | |
| <i>Pimephales</i> | 35,000 | 7 | | | | |
| <i>Physa</i> | 30,600 | 6 | | | | |
| <i>Acroeuria</i> | >22,600 | 5 | | | | |
| <i>Gammarus</i> | 22,000 | 4 | 0.3077 | 0.5547 | 9.9988 | 99.9760 |
| <i>Dugesia</i> | >16,600 * | 3 | 0.2308 | 0.4804 | 9.7172 | 94.4240 |
| <i>Crangonyx</i> @ | 9,190 | 2 | 0.1538 | 0.3922 | 9.1259 | 83.2821 |
| <i>Ceriodaphnia</i> | 2,648 | 1 | 0.0769 | 0.2773 | 7.8816 | 62.1196 |
| | | | 0.7692 | 1.7046 | 36.7235 | 339.8017 |

* Lowered to from >23,000 as correct value.

@ Added to the National Tox Database.

| | | | | |
|--------------------------|---|----------|---|----------|
| T | = | 4 | | |
| Σ ln (GMAV) | = | 36.7235 | S | = 7.8654 |
| Σ ln (GMAV) ² | = | 339.8017 | L | = 5.8290 |
| Σ P | = | 0.7692 | A | = 7.5877 |
| Σ Sq. Rt. (P) | = | 1.7046 | | |

Where Σ = Summation

A-C Ratio = 2.00 (Default Value, see 1988 EPA Criteria Document for Aluminum)
(*Daphnia* 51.47, *Ceriodaphnia* 0.9958, *Pimephales* 10.64, see 1988 EPA, Criteria Document, Table 2, Page 20)

| | | | | |
|-----|------------------------|-----------------|---|---|
| FAV | = eA (7.5877) | = 1973.770 ug/L | → | <u>Rounded Off Nos.</u> 1974 ug/L |
| AAC | = FAV/2 | = 986.885 ug/L | → | 987 ug/L |
| CAC | = FAV/A-C Ratio (2.00) | = 986.885 ug/L | → | 987 ug/L (174 ug/L)/* |

*/ Chronic Aquatic Criterion (CAC) = **174.00 ug/L**
(Lowered to protect Striped bass surrogate species- White bass- *Morone chrysops* and Largemouth bass- *Micropeterus* species etc., that are present in Indiana/ Midwest and beyond, see 1988 EPA Criteria Document for Aluminum, Page 6, Table 3, and Table 6 for Tox data)

U.S. EPA Calculated WQC for Aluminum:

FAV = 1496 ug/L
AAC (FAV/2) = 748 ug/L
CAC (FAV/Default A-C Ratio (2.00)) = 748 ug/L
Final Chronic Value (CAC) = **87.00 ug/L**
(Lowered to protect Brook trout and Striped bass, see 1988 EPA Criteria Document for Aluminum, Page 6 & Table 3.)

Ghias: March 2005

Aluminum Site-Specific WQC Calculations Details:

$$S^2 = \frac{\sum \{(\ln \text{GMAV})^2\} - \sum \{(\ln \text{GMAV})\}^2 / T}{\sum (P) - \sum \{(\sqrt{P})\}^2 / T}$$

$$S^2 = \frac{\sum \{(\ln 339.8017)^2\} - \sum \{(\ln 36.7235)\}^2 / 4}{\sum (0.7692) - \sum \{(\sqrt{1.7046})\}^2 / 4}$$

$$= \frac{339.8017 - 337.1539}{0.7692 - 0.7264}$$

$$= \frac{2.6478}{0.0428} = \sqrt{61.8645}; \quad S = 7.8654$$

$$L = \{ \sum (\ln \text{GMAV}) - S (\sum (\sqrt{P})) \} / T$$

$$L = \{ (36.7235) - 7.8654 \times 1.7046 \} / 4$$

$$= \{ 36.7235 - 13.4074 \} / 4$$

$$= 23.3161 / 4$$

$$= 5.8290$$

$$A = S \sqrt{0.05} + L$$

$$A = 7.8654 \times 0.2236 + 5.8290$$

$$= 1.7587 + 5.8290$$

$$= 7.5877$$

$$\begin{aligned} \text{FAV} &= e^A \\ &= e(7.5877) = 1973.77 \quad (1974) \end{aligned}$$